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Metal sulfides as a new class of sensing materials

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Abstract

In the recent years, metal sulfide nanostructured materials have become established in different research fields thanks to their excellent properties. Among the potential applications, metal sulfides may have a high standing role for gas sensing, in which, despite the wide assortment of sensing materials, still metal-oxides maintain a leading role because of their high sensitivity, low cost, small dimensions and simple integration. Experimentation carried out in this work with CdS and SnS_2 thick film sensors has showed an unexpected improvements of the chemoresistive properties with respect to their oxides counterparts, in particular toward selectivity to specific compounds, stability and the possibility to operate at room temperature. This opens towards the study of a novel class of sensing materials, which may solve the constant drift of the signal suffered by metal-oxides and ascribed to the in/out diffusion of oxygen vacancies, which alters the doping level.

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Keywords: CdS, SnS_2, stability, room temperature, thick films

1. Introduction

Gas sensors represent the crucial elements in specific analytes detection and olfactory systems for several applications: environmental monitoring, safety and security, quality control of food production, medical diagnosis and so on [1-3]. In order to satisfy an expanding demand for novel applications, gas sensors are under continuous

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evolution. Apart from the specific requirements of the applications, many other parameters have to be taken into account such as selectivity, processing costs, portability, and safety. So far the research in sensing materials, ranging from the well-known metal-oxide semiconductors [4] to conductive polymers [5] or organic-inorganic hybrids [6], has allowed producing highly performing devices. Concerning the chemoresistive gas sensors, a huge literature can be found on metal oxides semiconductors, due to their excellent sensitivity, fast response and recovery, and low-cost [7, 8]. However, despite their great advantages, metal oxides still exhibits unsolved drawbacks. In particular, their limited selectivity and lack of stability may result in long-term spoiling of the gas response. Moreover, these semiconductors often need a rather large amount of energy to support chemical reactions at the surface, activated at high temperatures that require non-negligible power consumption. In the search for novel sensing materials, the chemoresistive properties of two non-metal oxides were investigated in this work. Then, we led our research on cadmium sulfide (CdS) and tin disulfide (SnS_2), since the literature lacks of investigations on metal sulfides semiconductors thick-films for gas sensing applications. CdS and SnS_2, already studied as semiconductor films for solar cells [9, 10], were tested in thermo- and photo-activation modes. Each of these metal sulfides is the counterpart of a metal-oxide sensing material, in particular SnS_2 is the analogous of the widely used SnO_2, so the performances of two metal sulfides were compared with the respective metal-oxides.

2. Materials and methods

2.1 Powders synthesis and film preparation

Starting from the well-established experience of Sensors and Semiconductors Laboratory (SSL) [11], cadmium sulfide and tin disulfide (CdS and SnS_2) were synthetized as nanoparticles via precipitation reactions in aqueous solution, using thioacetamide as source of S^{2-} ions and metalorganic compounds to release metal ions. The pastes, obtained by thick-film technique, were screen-printed onto alumina substrates with interdigitated gold electrodes. Each metal sulfides is the counterpart of a metal-oxide sensing material: CdO, obtained as the result of a oxidization of CdS films after a thermal treatment, and SnO_2 synthetized by sol-gel technique. The chemical, morphological, structural and thermal properties of the as-synthesized materials and sensing films were investigated by XRD, SEM coupled with EDX, TEM, UV-Vis spectroscopy and TG analysis [12-15].

2.2 Gas measurements

The sensing properties of the devices were investigated in thermo- and photo- activation modes, performing conductance measurements in a suitable test chamber by means of the flow-through technique and testing several gases, at concentrations based on TLV STEL data, under dry and wet conditions. Temperature spectra were carried out for each metal sulfide sensor and, for both, it has proven that the best working temperature was 300 °C. In particular, for CdS, it was observed that a chemical reaction occurs at working temperature equal or higher than 400 °C. The thermal characterization showed an irreversible oxidation of CdS to CdO. Similarly, the thermal characterization highlighted that at temperatures higher than 300 °C the sulfur atoms and sulfur vacancies in SnS_2 are replaced with oxygen atoms, so it begins to transform into tin (II) oxide (SnS) and finally oxidizes to SnO_2. For this reason, 300 °C has to be considered the maximum operating temperature for SnS_2 for its stability. Measurements in photo-activation mode were carried out by means of LED with different wavelengths ranging from 400 to 645 nm. The response was calculated as the ratio of the difference between conductance in gas and in air, and conductance in air.

3. Results and discussion

CdS-based sensors showed a strong selectivity to alcoholic compounds at 300 °C (Fig. 1) [12], while CdO did not show any sensitivity to the several gases tested.

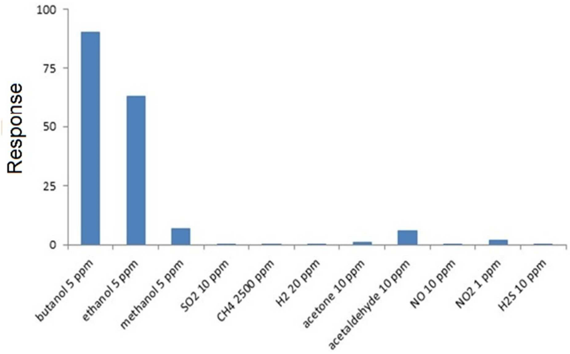

Fig. 1. Responses of CdS sensor to different gases analyzed at 300 °C.

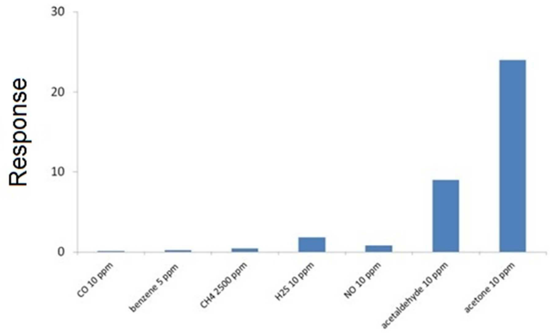

Fig. 2. Responses of SnS_2 sensor to different gases analyzed at 300 °C.

In photo-activation mode at room temperature, CdS showed a very important feature, i.e., the best sensing behavior was achieved with an excitation wavelength tuned on the bandgap energy. Ref. [12] reports a bandgap-resonant excitation of nanostructured CdS-based films which leads to an increase both in conductivity and in the surface chemical activity. Furthermore, the possibility to operate in photo-activation mode opens up to its possible use in low-consumption gas sensors. On the contrary, CdO [16] did not show interesting performance under photo-activation mode.

The same measurement protocol described before was used for SnS_2 and SnO_2 sensors. The former showed selectivity to ketones and aldehydes at relatively low temperature (Fig. 2) [15], whereas the sensitivity of SnS_2 to CO and CH_4 is well-known. On the contrary to CdS, SnS_2 did not show an electrical activity in photo-activation mode.

Figures 3 and 4 show the comparison between the response to ethanol (5 ppm) of CdS and CdO sensors, and to methane (2500 ppm) of SnS_2 and SnO_2 sensors, respectively.

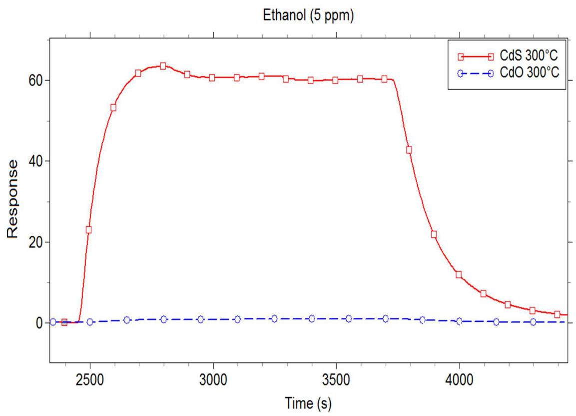

Fig. 3. Responses to ethanol (5 ppm) of CdS and CdO.

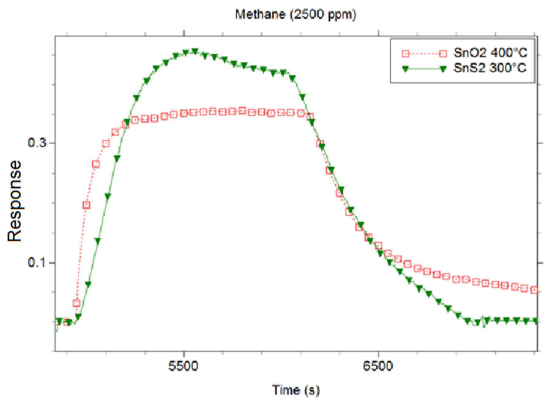

Fig. 4. Responses to methane (2500 ppm) of SnS_2 and SnO_2.

The performance of CdS and SnS_2 sensors are clearly better than those of their metal-oxides counterparts, not only for the significant sensitivity but also for response/recovery times and stability at a lower temperature. Then, with this metal sulfide, it is possible to operate in conditions which avoid oxidation of the film, obtaining a better stability with a lower power consumption than with the respective metal-oxide counterparts. This could be associated with a more significant thermodynamic equilibrium of oxygen at lower temperature for the metal sulphides than the oxides.

4. Conclusions

The metal sulfides tested in this study highlighted a very high selectivity and sensitivity to particular classes of molecules at a working temperature relatively lower than the classic metal oxide. In particular, CdS thick films also allows room temperature operation thanks to its photo-chemical properties. The responses of the sensors were reproducible over time, showing a particular stability of the signal. Therefore, the adoption on metal sulphide materials, where sulfur atoms replace of the oxygen, would pave the way to a sensitive, selective, and stable sensing material for gas detection.

Acknowledgements

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